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ELECTROMAGNETIC WAVE INTERACTIONS WITH METALLIC  
MICROPARTICLES: EXPERIMENTS WITH FIBERS AND FLAKES(U)  
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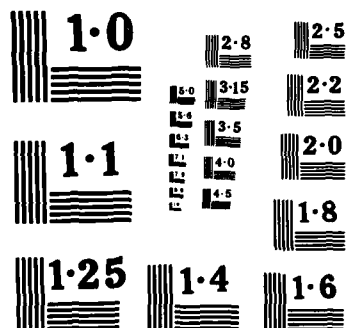
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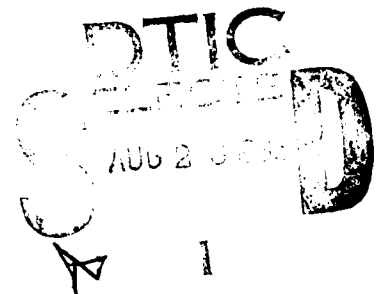
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ELECTROMAGNETIC WAVE INTERACTIONS WITH METALLIC MICROPARTICLES:  
EXPERIMENTS WITH FIBERS AND FLAKES

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19. KEY WORDS (Continue on reverse side if necessary and identify by block number) <div style="display: flex; justify-content: space-between;"> <div> <p>Surface enhanced Raman scattering,</p> <p>Electromagnetic enhancement,</p> <p>Charge-transfer enhancement,</p> <p>Electrochemical oxidation and reduction,</p> <p>Morphology-dependent resonances,</p> </div> <div> <p>Localized surface plasmons,</p> <p>Atomic scale roughness,</p> <p>S-1 photocathodes,</p> <p>Laser droplets,</p> <p>Colloids,</p> <p>Powder.</p> </div> </div>		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) <p>Metallic microstructures affect the surface electromagnetic intensity and the charge transfer between the metal and molecular adsorbates. Surface enhanced Raman scattering research has been conducted to further understand these two basic enhancement mechanisms on electrodes, colloids, powder, and S-1 photocathodes. Dielectric microstructures also affect the electromagnetic intensity, particularly inside the medium. In the case of optical fibers and liquid droplets, distinct morphology-dependent resonances can occur at specific ratios of the circumference to wavelength (size parameters). At these</p>		

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Resonances, a dielectric microstructure can be conceptualized as an optical cavity. Both linear and nonlinear laser scattering phenomena have been investigated when the monochromatic incident radiation and/or the broadband internally generated inelastic radiation are commensurate with these morphology-dependent resonances. Laser emission and stimulated Raman scattering from individual micron-size droplets have been observed for the first time. Originator  
Sullivan & Rogers to include

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## OBJECTIVES OF THE RESEARCH

The overall objective of the project was to initiate an experimental program to investigate electromagnetic interaction with metallic microparticles, particularly the effects of microparticle morphology, dielectric constants, and molecular overlayers on elastic and inelastic scattering properties in the near UV to the near IR. During the grant period, the following two specific objectives became the core of our experimental program: (1) surface enhanced Raman scattering (SERS) and surface enhanced nonlinear optical scattering from molecular adsorbates on roughened metallic electrodes, colloids, powder, and S-1 photocathodes containing Ag islands; and (2) nonlinear optical effects from dielectric microstructures, specifically liquid droplets.

## SUMMARY OF MAJOR RESEARCH RESULTS

### 1. Surface Enhanced Raman and Nonlinear Optical Scattering from Metallic Microstructures

The principal objective of the research on SERS and surface enhanced nonlinear optical scattering was to understand the underlying mechanisms which give rise to large enhancements when molecules are adsorbed on metallic microstructures of unspecified dimensions and shapes. Such metallic microstructures or roughness can be produced on electrodes by an electrochemical oxidation-reduction cycle, on colloids themselves by a chemical reduction process, on powder by oxidation and reduction reactions with an oxidizing gas such as  $\text{NO}_2$ , and on S-1 photocathodes by the evaporation of Ag metal.



The two dominant enhancement mechanisms are: (1) the electromagnetic effect involving localized surface plasmon resonances which are dependent on size and shape, as well as sensitive to the wavelength of the incident radiation and the metallic dielectric constant  $\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$ ; (2) the chemical effect involving an electron charge-transfer between the Fermi level of the metal and the electron affinity state of the molecule. Our work on the enhancement mechanisms was reported in publications 1, 2, and 3.

Of the two enhancement mechanisms, only the electromagnetic effect is amenable to calculations for discrete metallic microstructures with simple shapes, such as spheres and spheroids with a constant ratio of semi-major to semi-minor axes. The chemical effect, while not yet calculable, does manifest itself under specific experimental conditions such as potential cycling of the electrodes (see publications 4 and 5). It is surmised that potential cycling destroys the atomic scale roughness central to the chemical effect and leaves intact the larger scale roughness which is important to the electromagnetic effect. Although the causes are still not clear, experimental results indicate that laser illumination of the electrode during the oxidation half cycle and the presence of pyridine during the oxidation-reduction cycle further increase the SERS signal (see publications 6 and 7).

Since most SERS experiments with electrodes are performed in an aqueous electrolyte, we devoted considerable effort to the clarification of the necessary and sufficient conditions for observing the SERS of water. Why the SERS of minority species, such as 0.05 M pyridine,

could be readily detected while the SERS signal of 55 M water was unobservable was not clear prior to our research. Competition among the adsorbed species for surface sites on Ag electrodes was shown to be important, i.e., halide ions, pyridine and its halide complexes, and  $\text{H}_2\text{O}$  molecules can compete for the submonolayer of SERS active sites (see publication 8). The role of the metal cations ( $\text{Cs}^+$ ,  $\text{Rb}^+$ ,  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Li}^+$ ,  $\text{Ba}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$ ) in influencing the orientation of  $\text{H}_2\text{O}$  molecules adsorbed on active sites was investigated. For cations with larger hydration energy, the  $\text{H}_2\text{O}$  molecules are deduced to have their oxygen ends pointing away from the positively charged electrode. The cations with lower hydration energy leave the orientation of the  $\text{H}_2\text{O}$  molecules essentially intact, i.e., with their oxygen ends pointing toward the positively charged electrode (see publication 9). The role of the anions was also investigated, particularly the effect of high salt concentration on the SERS signal strength. High salt concentration in the aqueous electrolyte affects the SERS of  $\text{H}_2\text{O}$  in two ways: First, more anions can stabilize more SERS active sites. Second, more anions can break the hydrogen bonding between the adsorbed  $\text{H}_2\text{O}$  molecules and the rest of the water network beyond the first interfacial layer (see publication 10). The SERS of  $\text{OH}^-$  and  $\text{OD}^-$  is similar to the SERS of  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$ . In fact, cations and anions affect the hydroxyl ions in essentially the same way as they do water molecules (see publication 11). We have also used the second-harmonic generation from adsorbates and from Ag electrode surfaces themselves to distinguish the electromagnetic effect from the chemical effect. The lack of correlation between the SERS signal and the second-harmonic

signal as the electrode potential is swept led us to conclude that SERS is dominated by both the electromagnetic and chemical effects associated with the molecular adsorbates. The second harmonic is mainly dominated by the electromagnetic effect associated with the Ag surface itself and the thick AgX layer formed during the oxidation half cycle (see publication 12).

SERS can be observed on colloids as well as on electrode surfaces. We investigated the wavelength dependence of SERS from Ag colloids (see publication 13), Pt colloids (see publication 14), and Au colloids (see publication 15). The colloid shapes are nearly spherical and the radii are reasonably narrowly distributed. Hence, if the electromagnetic effect were the only mechanism or the dominant enhancement mechanism, the SERS wavelength dependence should agree with electromagnetic calculations on the surface-averaged enhancement factor. No definite conclusions could be made from our studies because in all colloids samples a small percentage of metallic clusters always exists. Consequently, while the extinction and elastic scattering spectra are dominated by nonaggregated colloids, it is conceivable that SERS excitation spectra are dominated by a few aggregated colloids. The electric fields between the aggregates can be extremely large and SERS is proportional to the fourth power of the electric field enhancement factor while the extinction and elastic scattering are proportional only to the second power of the electric field enhancement factor (see publication 13).

Metallic powder most closely resembles catalysts and thus provides a convenient bridge between laboratory samples and industrial catalysts.

SERS from Ag powder pre-exposed to  $\text{NO}_2$  gas was reported by us for the first time (see publications 16 and 17). The present understanding of SERS from Ag powder stems from our Ag electrode research. The SERS active sites from Ag powder are thought to be produced by the oxidation of metal Ag by the  $\text{NO}_2$  gas and subsequent autocatalytic reaction which causes Ag to be reduced, thereby forming the necessary Ag atomic scale roughness of each granule of Ag powder.

The S-1 photocathode is still the only efficient photocathode to convert near-IR radiation to electrons. Although this photocathode was discovered before World War II, the roles of the Ag islands and the form of the cesium suboxides are not clear even now. Our SERS studies have clarified the form of cesium suboxides surrounding the Ag microstructures for both S-1 and S-10 photocathodes. However, our research did not enable us to conclude whether or not the photoemission probability is increased by electromagnetic enhancements associated with the Ag morphology or by charge-transfer enhancements associated with electronic structure changes in small Ag islands (see publication 18).

## 2. Linear and Nonlinear Optical Effects from Dielectric Microstructures

Concurrent with our study of metallic microstructures, we investigated the effect of morphology on the elastic and inelastic spectra from optical fibers when the radiation is detected perpendicular to the fiber axis. It was noted by us, for the first time, that the Raman and fluorescence radiation emerging from glass fibers exhibits sharp peaks as a result of the cylindrical shape of fibers (see

publications 19 and 20). Such morphology-dependent resonances in the inelastic spectra can be predicted by the standard Lorenz-Mie theory for elastic scattering spectra. The inelastic radiation emitted from the dielectric microstructure is increased because of the glass-air interface. This increase is regardless of the scattering process, elastic or inelastic, coherent or incoherent, as long as the incident wavelength or the wavelengths of the internally generated inelastic radiation satisfy the appropriate condition for morphology-dependent resonance (i.e., specific size parameters  $2\pi a/\lambda$ , where  $a$  is the radius and  $\lambda$  is the wavelength).

In the case of nonlinear optical effects with intensity threshold dependence, the glass-air interface of a sphere can act as an optical cavity for the internally generated fluorescence or Raman radiation. At specific wavelengths within the fluorescence or Raman gain profile, the round-trip gain around the circumference can exceed the round-trip loss. Laser emission or stimulated Raman scattering thresholds can thereby be achieved. Our publications 21, 22, and 23 report the first observance of laser emission and stimulated Raman scattering from individual micron-sized droplets.

## PUBLICATIONS\*

Papers on surface enhanced Raman scattering (SERS) and surface enhanced nonlinear optical scattering from molecular adsorbates on roughened electrodes, colloids, powder, and S-1 photocathodes:

1. R.K. Chang, "Surface Enhancement Mechanisms," in Proceedings of the International Conference on Time-Resolved Vibrational Spectroscopy, 1982 (Academic Press, New York, 1983), p. 369.
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12. T.T. Chen, K.U. von Raben, D.V. Murphy, R.K. Chang, and B.L. Laube, "Surface Enhanced Raman Scattering and Second-Harmonic Generation from  $\text{CN}^-$  Complexes and  $\text{SO}_4^{2-}$  on Ag Electrodes during Oxidation Reduction Cycles, *Surf. Sci.* 143, 22 (1984).
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14. R.E. Benner, K.U. von Raben, K.C. Lee, J.F. Owen, R.K. Chang, and B.L. Laube, "Raman Scattering from  $\text{Pt}(\text{CN})_4^{2-}$  Adsorbed on Pt Colloids," *Chem. Phys. Lett.* 96, 65 (1983).
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Papers on linear and nonlinear optical effects from dielectric microstructures:

19. J.F. Owen, P.W. Barber, and R.K. Chang, "Morphology-Dependent Raman Spectra from Microparticles," in Microbeam Analysis 1982, K.F.J. Heinrich, ed. (San Francisco Press, 1982), p. 255.
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## SCIENTIFIC PERSONNEL

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